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TITLE: Thermosetting resin composition, cured resin
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BSPR:

On the other hand, in the fields of semiconductors such as condensers, diodes, transistors and integrated circuits such as IC, LSI, especially as sealing materials protecting mechanically and electrically semiconductors from outer environments, epoxy resins are mainly used at the present time. However, in these applications, there also exists a problem that internal stress is generated due to a difference in linear expansion coefficient between epoxy resins and silicon chips or lead frames or due to strain on curing. This internal stress causes defects and cracks in protective films for semiconductor elements and furthermore, cracks in semiconductor elements themselves. Moreover, this internal stress causes strains in lead frames, which tends to cause poor insulation between frames.

BSPR:

A terminally active polymer in accordance with the invention which is useful in preparing such resin compositions is a polyimide, polyamide or polyether, which polymer is derived from at least two reactants capable of providing, in the polymer, respective residues (a) and (b) of the formula ##STR1## wherein R.sub.1 and R.sub.2 are, independently of one another, each selected from hydrogen and a group C.sub.m H.sub.2m+1, where m is at least 1, and ##STR2## wherein R.sub.2 is a hydrocarbyl group (optionally interrupted by a hetero

atom), R.sub.3 is a hydrocarbylene-radical (optionally interrupted by a hetero atom) and n is from 1 to 20 inclusive. Preferably R.sub.2 is a C.sub.1-4 alkyl or phenyl group and R.sub.3 is a C.sub.1-4 alkylene or phenylene group. A preferred value of m is from 1 to 4 inclusive. The groups R.sub.1 and R.sub.1 ' are preferably hydrogen.

DEPR:

The component (A) in a resin composition of the present invention is a thermosetting resin. As the thermosetting resin used in the present invention, any resin which can be cured by means of an external energy such as heat, light or electron beam to form at least partially a three dimensional cured product can be used and no limitation exists. As the thermosetting resins which are especially suitable for products of the present invention, epoxy resins are first mentioned. Especially preferred are those epoxy resins which are prepared from precursors such as amines, phenols and compounds having a carbon-carbon double bond. Practically, examples of the epoxy resins whose precursors are amines are tetraglycidyl-diaminodiphenylmethane, triglycidyl-p-aminophenol, triglycidyl-m-aminophenol and triglycidylaminocresol and their isomers, examples of the epoxy resins whose precursors are phenols are bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, phenol-novolak epoxy resins, cresol-novolak epoxy resins and resorcinol epoxy resins, and examples of the epoxy resins whose precursors are compounds having a carbon-carbon double bond are alicyclic epoxy resins. Moreover, brominated epoxy resins prepared by brominating these epoxy resins can be used, but the present invention is not restricted to the use of these compounds. Furthermore, mixtures of two or more of the epoxy resins

can be used and monoepoxy compounds can be also incorporated.

DEPR:

Moreover, thermosetting polyimide resins having a terminal reactive group are also suitable for the component (A). As the terminal reactive group, nadiimide group, acetylene group and benzocyclobutene group are preferable.

DEPR:

One of the preferred examples is a block copolymer or a graft copolymer having a molecular chain consisting of a siloxane skeleton which is originally incompatible with the component (A) or (B) and has high toughness and low water absorption ratio. An especially preferred example is a block copolymer or a graft copolymer wherein the part other than the molecular chain consisting of a siloxane skeleton consists of a polyimide skeleton, a polyamide skeleton or a polyether skeleton which is compatible with the component (A) or (B). Moreover, it is especially preferred that this block copolymer or graft copolymer has a terminal functional group which is reactive with the constitutional element (A) or (B).

DEPR:

Furthermore, a bulky structure in the polyamide skeleton, the polyimide skeleton or the polyether skeleton is preferred as it improves solubility in the component (A) or (B). One of the practical examples of such a bulky structure is a structure of formula I ##STR6## (wherein R.sub.1 and R.sub.1' are each, independently of one another, selected from H and CmH.sub.2 H.sub.2m+1 ; m is at least 1).

DEPR:

A block copolymer or a graft copolymer preferable as the component (C) has for

example a polyimide molecular chain. A polyimide having a siloxane chain is per se known, this having been reported by J. E. McGrath at the 32nd SAMPE Symposium P.613 (1978), but there is no example wherein this compound is used for improving toughness of a cured resin product obtained, for example, from an epoxy resin. As one of the reasons for this, it is believed that this type of polyimide is not dissolved in epoxy resins and therefore, uniform mixing with the desired resin could not be obtained (as the present inventors have also confirmed by experiments). However, the present inventors have succeeded in incorporating the siloxaneimide into cured resin products from, for example, epoxy resins by copolymerising with a diamine of the formula I, given and defined above.

DEPR:

The polyimide chain part can be synthesised using a monomer of the following structural formula, but the copolymers used in the present invention are not restricted to these. ##STR8##

DEPR:

218 g (0.75 mol) of 1,3-bis(3-aminophenoxy)benzene (APB), 33 g (0.094 mol) of 9,9'-bis(4-aminophenyl)fluorene (FDA), and 122 g (0.094 mol) of amino-terminated dimethyl siloxane having an NH.sub.2 equivalent of 650 (commercially available from Toray Silicone Co., Ltd., BY-16-853) were stirred and dissolved in 2,000 ml of N-methyl-2-pyrrolidone (NMP) in a separable flask of 3,000 ml equipped with a nitrogen inlet, a thermometer, a stirrer and a trap for dehydration under nitrogen substitution. 250 g (0.85 mol) of solid biphenyltetracarboxylic dianhydride were added bit by bit and the mixture was stirred at room temperature for 3 hr and after elevating the temperature up to

120.degree. C., the mixture was stirred for 2 hr. After the temperature of the flask was returned to room temperature and 50 ml of triethylamine and 50 ml of toluene were added, the temperature was elevated again and azeotropic dehydration was carried out at 160.degree. C. to obtain about 30 ml of water. Thereafter, this reaction mixture was cooled, diluted with double the amount of NMP and poured slowly into 20 ml of acetone to precipitate an amine-terminated siloxane polyimide oligomer as a solid product.

DEPR:

28.7 g of siloxane polyimide oligomer obtained in part A and 50 g of resorcinol diglycidyl ether (commercially available from Wilmington Chemical Co., Ltd., HELOXY WC-69) were placed in a beaker. The mixture was heated and dissolved at 150.degree. C. for 2 hr and 23.7 g of 4,4'-diaminophenyl sulfone (DDS) were added and dissolved for 10 min.

DEPR:

As component (C), 40 g of the siloxane polyimide oligomer of Example 1 Part a, 21.5 g of resorcinol diglycidyl ether (commercially available from Wilmington Chemical Co., Ltd., HELOXY WC-69) and 21.5 g of bisphenol F diglycidyl ether (commercially available from Dainippon Ink and Chemicals Inc., Epichlon 830) were mixed in a beaker. The mixture was heated and dissolved at 150.degree. C. for 2 hr and then 16.7 parts of 4,4'-diaminodiphenyl sulfone (DDS) were added and allowed to dissolve for 10 min.

DEPR:

As a component (C), 30 g of the siloxane polyimide oligomer of Example 1 Part A was added to 39 g of diphenylmethanebismaleimide and 31 g of o,o'-diallylbisphenol A and heated and dissolved at 150.degree. for 2 hr.

DEPR:

392 g (0.91 mol) of bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-M), 39 g (0.11 mol) of 9,9'-bis(4-aminophenyl)fluorene (FDA), 147 g (0.11 mol) of an amino-terminated dimethyl siloxane having an NH group equivalent of 650 (commercially available from Toray Silicone Co., Ltd., BY-16-853) and 300 g (1.02 mol) of biphenyltetracarboxylic dianhydride were used as the raw materials. Other procedures were the same as those of Example 1 to synthesize a siloxane polyimide oligomer.

DEPR:

30 g of siloxane polyimide oligomer obtained in Part A, 25 g of resorcinol diglycidyl ether and 25 g of phenol-novolak epoxy resin (Epicoat 152 manufactured by Yuka Shell Epoxy Co., Ltd.) were added to a beaker and heated and dissolved. Then, 20 g of 4,4'-diaminodiphenyl sulfone (DDS) were added. The same procedures as those of Example 1 were repeated. The T_g of the obtained cured resin was 185.degree. C. The release rate of fracture strain energy GIC was 1,500 J/m² and the bending elastic modulus was 300 Kg/mm². The water absorption ratio measured by boiling a resin sheet of 60.times.10.times.2 mm for 20 hr was 2.5%.

DEPR:

208 g (0.712 mol) of bis(3'-aminophenoxy)benzene (APB) and 62 g (0.178 mol) of 9,9'-bis(4-aminophenyl)fluorene (FDA) were stirred and dissolved in 2,000 ml of N-methyl-2-pyrrolidone (NMP) in a separable flask of 3,000 ml equipped with a nitrogen inlet, a thermometer, a stirrer and a trap for dehydration under nitrogen substitution. 240 g (0.816 mol) of solid biphenyltetracarboxylic dianhydride were added bit by bit and the mixture was stirred at room temperature for 5 hr. Thereafter, 50 ml of triethylamine

and 50 ml of toluene were added, the temperature was elevated again and azeotropic dehydration was carried out at 160.degree. C. to obtain about 30 ml of water. After this reaction mixture is cooled, it was diluted with double the amount of NMP and poured slowly into 20 ml of acetone to precipitate an amine-terminated polyimide oligomer as a solid product. This precipitate was vacuum-dried at 200.degree. C. The number average molecular weight (Mn) of this oligomer was measured by means of gel permeation chromatography (GPC) by using dimethyl-formamide (DMF) as a solvent and was found to be 5,000 in terms of polyethylene glycol (PEG). The glass transition temperature determined by means of a differential scanning calorimeter (DSC) was 210.degree. C. The amine terminal was confirmed by means of NMR spectra and IR spectra.

DEPR:

28.7 g of polyimide oligomer obtained in part A and 50 g of resorcinol diglycidyl ether (commercially available from Wilmington Chemical Co., Ltd., HELOXY WC-69) were added in a beaker. The mixture was heated and dissolved at 150.degree. C. for 2 hr and then 23.7 g of 4,4'-diaminodiphenyl sulfone (DDS) were added and dissolved for 10 min.

CLPR:

1. A cured resin product comprising a thermoset resin (A) and a thermoplastic resin (C), wherein the cured resin product comprises at least a phase (1) in which the thermoplastics resin (C) is at least a major constituent; and a phase (2) in which the thermoset resin (A) is at least a major constituent, each of said phases (1) and (2) is separate from the other and has a three dimensionally continuous structure, and phase (1) contains a silicon containing

compound and has a concentration of elemental silicon higher than that in any other phase, wherein the cured resin product is formed from a thermoplastics resin (C) comprising a copolymer selected from the group consisting of block and graft copolymers, which copolymer has a siloxane molecular chain originally incompatible with, and a molecular chain selected from the group consisting of polyimide, polyamide and polyether molecular chains compatible with, the thermoset resin (A), wherein the thermoset resin (A) comprises a resin selected from the group consisting of epoxy, maleimide, triazine, polyimide and phenol resins, and combinations thereof, cured with a curing agent (B), and the thermoplastics resin (C) has terminal groups chemically combined with the thermoset resin (A), wherein the thermoplastics resin (C) additionally contains residues having a structure (a) ##STR9## where R.sub.1 and R.sub.1 ' are, independently of one another, each selected from H and a group C.sub.m H.sub.2m+1, where m is at least 1.

CLPR:

2. A resin composition comprising a thermosetting resin (A), a curing agent B) and a thermoplastics resin (C), which is soluble in the resin (A), wherein the thermoplastics resin (C) is a copolymer selected from the group consisting of block copolymers and graft copolymers each comprising a molecular chain compatible with, and a molecular chain incompatible with, at least one of the thermosetting resin (A) and curing agent (B) wherein the thermoplastic resin (C) is selected from the group consisting of polyimides, polyamides and polyethers each having a siloxane molecular chain, wherein the thermoplastics resin (C) additionally contains residues having a structure of formula (a) ##STR10## where R.sub.1 and R.sub.1 ' are, independently of

one another, each
selected from H and a group $C_{sub.m} H_{sub.2m+1}$, where m is
at least 1.

CLPR:

3. A cured resin product comprising a thermoset resin (A)
and a thermoplastic
resin (C), wherein the cured resin product comprises at
least a phase (1) in
which the thermoplastics resin (C) is at least a major
constituent; and a
phase (2) in which the thermoset resin (A) is at least a
major constituent,
each of said phases (1) and (2) is separate from the other
and has a three
dimensionally continuous structure, and phase (1) contains
a silicon containing
compound and has a concentration of elemental silicon
higher than that in any
other phase, wherein the cured resin product is formed from
a thermoplastics
resin (C) comprising a copolymer selected from the group
consisting of block
and graft copolymers, which copolymer has a siloxane
molecular chain originally
incompatible with, and a molecular chain selected from the
group consisting of
polyimide, polyamide and polyether molecular chains
compatible with, the
thermoset resin (A), wherein the thermoplastics resin (C)
is selected from the
group consisting of polyimides and polyamides each having a
siloxane molecular
chain.

CLPR:

4. A cured resin product according to claim 3, wherein the
thermoplastic resin
is a polyimide having a siloxane molecular chain.

CLPR:

5. A cured resin product comprising a thermoset resin (A)
and a thermoplastic
resin (C), wherein the cured resin product comprises at
least a phase (1) in
which the thermoplastics resin (C) is at least a major
constituent; and a
phase 2) in which the thermoset resin (A) is at least a

major constituent, each of said phases (1) and (2) is separate from the other and has a three dimensionally essentially continuous structure, and the cured resin product additionally includes regions where one of the phases (1) and (2) essentially surrounds the other, wherein the cured resin product is formed from a thermoplastics resin (C) comprising a Copolymer selected from the group consisting of block and graft copolymers, which copolymer has a siloxane molecular chain originally incompatible with, and a molecular chain selected from the group consisting of polyimide, polyamide and polyether molecular chains compatible with, the thermoset resin (A), wherein the thermoplastics resin (C) is selected from the group consisting of polyimides and polyamides each having a siloxane molecular chain.

CLPR:

6. A cured resin product according to claim 5, wherein the thermoplastic resin is a polyimide having a siloxane molecular chain.

CLPR:

7. A cured resin product having a thermoset resin (A) and a thermoplastic resin (C), wherein the cured resin product is formed from a thermoplastics resin (C) comprising a copolymer selected from the group consisting of block and graft copolymers, which copolymer has a siloxane molecular chain originally incompatible with, and a molecular chain selected from the group consisting of polyimide, polyamide and polyether molecular chains compatible with, the thermoset resin A); wherein said cured resin product has a strain energy release rate (GIC) of at least 400 J/m^2 , a flexural modulus of at least 300 Kg/mm^2 , a glass transition temperature (T_g) of at least 120°C ., at least two phases, each of which phases has a three

dimensionally continuous structure, and one of which phases contains a silicon containing compound and has a concentration of elemental silicon higher than in any other phase, wherein the thermoplastics resin (C) is selected from the group consisting of polyimides and polyamides each having a siloxane molecular chain.

CLPR:

8. A cured resin product according to claim 7, wherein the thermoplastic resin is a polyimide having a siloxane molecular chain.

CLPR:

9. A cured resin product comprising a thermoset resin component (A) and a thermoplastics resin component (C), Said thermoplastics resin and thermoset resin component (C) and (A) being present at least partly in respective phases (1) and (2), each of said phases being continuous and one of said phases (1) and (2) contains a silicon containing compound and has a concentration of elemental silicon higher than that in any other phase, wherein the cured resin product is formed from a thermoplastics resin (C) comprising a copolymer selected from the group consisting of block and graft copolymers, which copolymer has a siloxane molecular chain originally incompatible with, and a molecular chain selected from the group consisting of polyimide, polyamide and polyether molecular chains compatible with, the thermoset resin (A), wherein the thermoplastics resin (C) is selected from the group consisting of polyimides and polyamides each having a siloxane molecular chain.

CLPR:

10. A cured resin product according to claim 9, wherein the thermoplastic resin is a polyimide having a siloxane molecular chain.

CLPR:

11. A resin composition comprising a thermosetting resin (A), a curing agent (B) and a thermoplastics resin (C), which is soluble in the resin (A), wherein the thermoplastics resin (C) is a copolymer selected from the group consisting of block copolymers and graft copolymers each comprising a molecular chain compatible with, and a molecular chain incompatible with, at least one of the thermosetting resin (A) and curing agent (B), wherein the thermoplastics resin (C) is selected from the group consisting of polyimides and polyamides each having a siloxane molecular chain.

CLPR:

12. A resin composition according to claim 11, wherein the thermoplastic resin is a polyimide having a siloxane molecular chain.